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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification 6 :</b> <b>D01F 9/127, 9/133</b>		<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/58748</b> <b>(43) International Publication Date:</b> 18 November 1999 (18.11.99)
<b>(21) International Application Number:</b> PCT/US99/10552		<b>(81) Designated States:</b> JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
<b>(22) International Filing Date:</b> 12 May 1999 (12.05.99)		<b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
<b>(30) Priority Data:</b> 09/078,187 13 May 1998 (13.05.98) US			
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**(54) Title:** PLASMA CATALYSIS OF CARBON NANOFIBERS

**(57) Abstract**

A process for forming carbon nanofibers by means of pyrolyzation with plasma in a reactor is disclosed. The process includes the steps of: providing, in a reactor, a first catalyst in the form of solid catalytic particles; applying a vacuum to the reactor to create a reduced pressure in the reactor; feeding a first mixture of gases including a carbon-based gas into the reactor; forming, from the carbon-based gas, a plasma containing carbon free-radical species; and forming, in the presence of the catalytic particles, carbon nanofibers.

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## PLASMA CATALYSIS OF CARBON NANOFIBERS

### BACKGROUND OF THE INVENTION

The present invention relates to a method for forming carbon nanofibers, which are also known as nanotubes, by means of a generated plasma 5 and chemically assisted catalysis.

Carbon fibers hold great promise as a high-performance material for use in composites due to their high strength and high modulus. They are commonly made by elevating a precursor material such as polyacrylonitrile (PAN) or pitch in an inert atmosphere to a temperature around 1000°C on continuous wind-up devices.

10 The fibers formed by this process are generally continuous filaments and approximately 8µm in diameter.

Recently, carbon nanofibers have been produced directly from hydrocarbons in a gas phase reaction upon contact with a catalytic metal particle when heated by thermal energy to around 1000°C in a non-oxidizing gas stream.

15 Carbon nanofibers differ physically from commercial carbon fibers in that they are thinner and are not continuous. Typically, they have a length around 0.01 mm to 0.1 mm and have a diameter generally of 10nm to 100nm. Carbon nanofibers also differ functionally from commercial carbon fibers in that they have a higher thermal conductivity, have high electrical conductivity, and are less subject to etching.

20 Accordingly, carbon nanofibers offer great promise in a number of applications.

Carbon nanotubes are structures which consist of a sheet of carbon atoms in graphene forms wrapped into a cylinder. A single walled nanotube has only a single atomic layer. Multiwalled nanotubes have additional layers of carbon deposited pyrolytically. Multiwalled nanotubes may thus contain 100 to 1000 atomic 25 layers. Multiwalled nanotubes have excellent strength, small diameter (typically less than 200 nm) and near-metallic electrical conductivity, making them useful as an additive to enhance structural properties of composites such as carbon-carbon, carbon-epoxy, carbon-metal, carbon-plastic, carbon-polymer and carbon-concrete.

-2-

Carbon nanotubes have been produced by arc-evaporation chemical reactions and by pyrolysis reactions using lasers to initiate pyrolysis. However, these methods are not effective for producing significant quantities of nanofibers. Thus, a need exists in the art for a method which can reliably and effectively produce carbon 5 nanofibers in significant quantities.

### SUMMARY OF THE INVENTION

The present invention provides a method for making carbon nanofibers and nanotubes which is quick and efficient. By being quick and efficient, it has the potential to be less expensive than currently used methods.

10 In one aspect of the process present invention, carbon nanofibers are formed in a reactor. The process includes the steps of: providing, in a reactor, a first catalyst in the form of solid catalytic particles; applying a vacuum to the reactor to create a reduced pressure in the reactor; feeding a first mixture of gases including a carbon-based gas into the reactor; forming, from the carbon-based gas, a plasma 15 containing carbon free-radical species; and forming, in the presence of the catalytic particles, the carbon free-radical species into carbon nanofibers. Desirably, the first mixture of gases also includes hydrogen gas which is provided to inhibit pyrolytic fattening of the carbon nanofibers and to inhibit the formation of soot during the reaction. It is also desirable that the process includes the additional step of feeding a 20 growth catalyst gas into the reactor to cause the fibers to increase diametrically in size.

The carbon nanofibers of the present invention can be further processed to form a carbon-carbon matrix material. To form a carbon-carbon matrix material, the process includes the following additional steps: increasing the 25 concentration of the carbon-based gas in the first mixture of gases to form a second mixture of gases; pyrolyzing the second mixture of gases to deposit a bulk layer of carbon on the carbon nanofibers forming a carbon-carbon matrix material which contains carbon nanofibers throughout its thickness; and removing the matrix material from the reactor.

-3-

In another aspect of the process of the present invention, a gaseous catalyst can be used to facilitate formation of the carbon nanofibers. This aspect of the process includes the following steps: applying a vacuum to the reactor to create a reduced pressure in the reactor; feeding a mixture of gases including a carbon-based gas into the reactor; feeding a catalyst gas into the reactor; forming, from the carbon-based gas, a plasma containing carbon free-radical species; and forming, in the presence of the catalyst gas, the carbon free-radical species into carbon nanofibers. Desirably, the mixture of gases also includes hydrogen gas which is provided to inhibit pyrolytic fattening of the carbon nanofibers as they are being formed and to inhibit the formation of soot during the reaction. It is also desirable with the process that the process also includes the additional step of feeding a growth catalyst gas into the reactor to cause the fibers to increase diametrically in size.

The carbon nanofibers of the present invention can be further processed to form a carbon-carbon matrix material. To form a carbon-carbon matrix material, the process includes the following additional steps: increasing the concentration of the carbon-based gas in the first mixture of gases to form a second mixture of gases; pyrolyzing the second mixture of gases to deposit a bulk layer of carbon on the carbon nanofibers forming a carbon-carbon matrix material which contains carbon nanofibers throughout its thickness; and removing the matrix material from the reactor.

The present invention is also directed to a process for forming a carbon-epoxy matrix material. This process comprises the following steps: providing, in a reactor, solid catalyst particles on a substrate; feeding a mixture of gases including a hydrogen gas and a carbon-based gas into the reactor; forming, from the carbon-based gas, a plasma containing carbon free-radical species; forming, in the presence of the catalytic particles, the carbon free-radical species into carbon nanofibers; removing the substrate bearing the carbon nanofibers from the reactor; forming a mold in which a portion of the mold is formed by the substrate; infiltrating the mold with an epoxy composition to form a carbon-epoxy matrix material.

containing carbon nanofibers throughout its thickness; and removing the matrix material from the mold.

Objects and advantages of the present invention will be apparent from the following detailed description, the accompanying drawings and the appended 5 claims.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a photomicrograph of the carbon nanostructures formed by the process of this invention.

Fig. 2 is a photomicrograph showing the crosslinking of the carbon 10 nanostructures formed by the process of this invention.

Fig. 3 is a schematic representation of the equipment used to produce carbon nanostructures via microwave dissociation.

#### DETAILED DESCRIPTION OF THE INVENTION

The method of this invention produces carbon nanostructures such as 15 those shown in Figs. 1 and 2. Fig. 1 is a photomicrograph at 750X magnification and Fig. 2 is a photomicrograph at 15,000X magnification. The fibers, shown in Figs. 1 and 2, have a diameter of about 100 nm, which is about three orders of magnitude smaller than conventional pitch or PAN-based fibers. For that reason, these fibers are referred to as being "nanofibers." The fibers typically have a length of about 1-2 20 mm. Thus, they have an aspect ratio (L/d) of about  $1 \times 10^4$  and a surface area to volume ratio of about  $1 \times 10^{14} \text{ m}^{-1}$ . Further, as can be seen in Fig. 2, the individual fibers tend to cross-link with each other which increases the capacity of the fibers to conduct heat and electricity. These fibers also have a high level of graphitization which further increases their high thermal conductivity and provides near-metallic 25 electrical conductivity.

The carbon nanofibers are formed by a chemical catalysis of a plasma formed from a carbon-based gas. The plasma is formed by means of the plasma generator. Typically, the plasma generating source is a microwave generator, a hot

filament, an RF generator or an electrical discharge. This differs from the prior art which uses thermal energy sources, such as lasers, or chemical sources to form carbon nanofibers.

To form the fibers, a mixture of gases, including the carbon-based gas, 5 are provided in a reactor. Typically, these gases, which form the mixture, are fed into the reactor from tanks containing the respective gases. The formation of the fibers is carried out at a reduced pressure of from about 10 Torr to about 100 Torr and, desirably, from about 20 Torr to about 50 Torr. The carbon-based gas is formed into a plasma in the presence of a first catalyst in the reactor. The mixture of gases can 10 be formed into a plasma by means of a plasma generating source such as a microwave generator, a hot filament, an RF generator or an electrical discharge. The first catalyst can be either in the form of solid catalytic particles or in a gaseous state. If a solid catalyst is used, it is placed on a substrate in the reactor. If a substrate is used, the substrate has a temperature from about 800°C to about 1200°C and, 15 desirably, a temperature from 800°C to about 1000°C. Desirably, the mixture of gases also includes hydrogen gas. The hydrogen gas is provided to inhibit pyrolytic fattening of the nanofibers and to inhibit the formation of soot during the pyrolysis reaction. Once the plasma has been formed from the carbon-based gas, carbon nanofibers are formed by the chemically catalyzed deposition of carbon from the 20 carbon free-radical species generated in the plasma. A second catalyst in the form of a growth catalyst gas may also be used to promote diametric growth of the fibers.

In the plasma, carbon atoms are dissociated from the carbon-based gas and a plasma is formed which contains carbon and hydrocarbon free-radicals. Then the carbon is captured by the catalyst to form the carbon nanofibers. The entire 25 process requires no more than about one hour of time from start to finish.

The carbon-based gas must be a gas which forms carbon and hydrocarbon free-radical species upon pyrolysis. Desirably, the carbon-based gas used to form the carbon fibers is at least one gas selected from the group consisting of carbon dioxide, methane, ethane, propane, ethene, natural gas and coal derivative 30 gases. The carbon-based gas may also be a mixture of these gases. More

desirably, the carbon-based gas is methane. Desirably, the gas mixture used to form the carbon fibers includes from about 40% to about 90% of hydrogen gas and from about 10% to about 60% of the carbon-based gas. More desirably, the gas mixture comprises about a 50-50 mixture of hydrogen gas and the carbon-based gas.

5 Typically, the gas flow for the fiber formation reaction measures from about 20 sccm to about 1000 sccm and desirably is about 100 sccm.

In one aspect of the process of the present invention, to initiate formation of the nanofibers, the first catalyst is provided in the form of solid particles having a size from about 10 nm to about 1 micron. The first catalyst is selected from 10 the group consisting of iron containing materials, nickel containing materials, cobalt containing materials and sulfur containing materials. Useful materials for the first catalyst include, but are not limited to, iron, nickel, cobalt, ferrocene, iron pentacarbonyl, alloys of iron, alloys of nickel, alloys of cobalt, sulfur, hydrogen sulfide, iron sulfide, and nickel nitrate. Desirably, the first catalyst is iron sulfide. It is believed 15 that the particles of the first catalyst serve to nucleate the fibers and cause the beginning of fiber formation. Typically, from about 10 mg to about 100 mg of the first catalyst in the form of particles is used to form 10 mg of fibers.

In a more desired version of this aspect of the invention, a second, growth catalyst gas may also be used in combination with the hydrogen gas and the 20 carbon-based gas to modify the surface properties of the fibers. The growth catalyst is applied to "fatten" the fibers, i.e., it is a second catalyst which promotes diametric growth of the fiber. Useful growth catalysts include hydrogen, ammonia and mixtures thereof. Desirably, the growth catalyst will be ammonia.

In another aspect of the process of the present invention, the first 25 catalyst can be provided in a gaseous state rather than being provided as solid particles. If the first catalyst is used in a gaseous state, it may be supplied in combination with the hydrogen gas and the carbon-based gas simultaneously as a mixture of gases. In this reaction, the carbon nanofibers are produced on a steady state basis and are collected as they form. If the first catalyst is in the gaseous form,

it will be selected from the group consisting of iron pentacarbonyl, hydrogen sulfide, and a ferrocene-xylene mixture.

A deposition apparatus 10 useful for forming the carbon nanofibers shown in Figs. 1 and 2 is shown in Fig. 3. The apparatus 10 comprises a plasma 5 reactor 12, a series of gas tanks 14, and a vacuum pump 16. Gas tanks 14 feed gas into reactor 12 and pump 16 is provided to create a reduced pressure in reactor 12. Reactor 12 is desirably a microwave reactor such as an ASTEX microwave reactor available from Applied Science and Technology of Woburn, Massachusetts, U.S.A. Pump 16 can be a conventional mechanical vacuum pump. A useful vacuum pump is 10 available from Varian Vacuum Products of Lexington, Massachusetts, U.S.A. Pump 16 desirably includes an associated pressure measuring device, which is desirably a baratron device.

Reactor 12 includes a power supply 20, a feed tube 22 and a waveguide 24. Power supply 20 provides reactor 12 with a source of energy. 15 Desirably, reactor 12 is a microwave reactor and power supply 20 is a microwave generator. Thus, the energy source used to form the plasma from the carbon-based gas is desirably microwave energy. Feed tube 22 is disposed in reactor 12 and extends generally axially therein. Desirably, feed tube 22 extends along more than  $\frac{1}{2}$  of the length of reactor 12 and more desirably extends along more than  $\frac{3}{4}$  of the 20 length of reactor 12. Waveguide 24 extends from power supply 20 to feed tube 22. Waveguide 24 directs energy from power supply 20 to feed tube 22. Reactor 12 and feed tube 22 are desirably constructed of a material which is resistant to heat and corrosion. Suitable materials include nickel, high temperature steel, quartz, ceramic, and refractory materials. Desirably, feed tube 22 is formed from quartz. An optional 25 catch basin 46 may be positioned at one end of feed tube 22. Catch basin 46 is used to collect fibers formed when the first catalyst is a gas.

Gas tanks 14 include a hydrogen gas tank 30, a carbon-based gas tank 32, an optional tank 34 for containing the growth catalyst, and an optional tank 36 for containing a gaseous catalyst. Gas tanks 30, 32, 34 and 36 are connected to feed

tube 22 by a series of gas lines 38. Control of the flow of gas from tanks 30, 32, 34 and 36 is provided by a series of mass flow controllers 40.

To monitor the temperature of the reaction which forms the carbon fibers, the apparatus 10 may also include an optical pyrometer 42. Pyrometer 42 is 5 used instead of a thermocouple because thermocouples are susceptible to interaction with the field of plasma generated in reactor 12.

When the first catalyst is in the form of solid catalytic particles, a substrate (not shown) is used to support the first catalyst in reactor 12. The substrate is desirably formed from an inert dielectric material such as quartz, ceramic and 10 refractory materials. Desirably, the substrate is ceramic. Metals, such as molybdenum, titanium and nickel may also be used.

The first catalyst, in the form of solid catalytic particles, is placed on the substrate which is then positioned in feed tube 22. The substrate and first catalyst particles are positioned so that they are positioned in about the center of feed tube 22 15 at the intersection of waveguide 24 and feed tube 22. The substrate can be positioned in feed tube 22 on a rod which is desirably an aluminum oxide rod. After the substrate and associated first catalyst particles have been positioned in feed tube 22, the pressure in feed tube 22 is reduced by means of vacuum pump 16. A total 20 vacuum is not created in feed tube 22 but the pressure is reduced to a pressure measuring from about 10 Torr to about 100 Torr and, desirably, from about 20 Torr to about 50 Torr. The gases from the hydrogen gas tank 30 and carbon-based gas tank 32 are fed through the gas lines 38 and combined to form a mixture of gases which is fed from tanks 14 through gas lines 36 to feed tube 22. As stated above, mass flow 25 controllers 40 control the flow of gases from tanks 14 to feed tube 22. Typically, the gas flow will be provided at a rate from about 20 sccm to about 1000 sccm and desirably at about 100 sccm.

As the mixture of gases flows into feed tube 22 and passes waveguide 24, it is subjected to a flow of energy emitted from power supply 20 of reactor 12 and is formed by the heat energy generated by the power supply 20 into a plasma 30 containing carbon free-radicals, hydrogen free-radicals, hydrocarbon free-radicals,

and oxygen free-radicals, if an oxygen containing gas is used. The energy is conveyed from power supply 20 to feed tube 22 through waveguide 24. To generate the plasma, power supply 20 requires from about 600 Watts to about 1200 Watts of power. Once the desired amount of fibers have been formed, the flow of energy from 5 power supply 20 is discontinued, the gas flow is ceased and the fibers are removed from the reactor 12. When a growth catalyst gas is employed in the reaction, the growth catalyst gas is supplied from tank 34 simultaneously with the hydrogen gas and the carbon-based gas in the mixture of gases.

In another version of the process of this invention, the first catalyst can 10 be provided to feed tube 22 in a gaseous state rather than being provided as solid particles. If the first catalyst is used in a gaseous state, it will be provided from tank 36 through gas lines 38 to feed tube 22. It may be supplied to feed tube 22 in combination with the hydrogen gas and the carbon-based gas simultaneously as a mixture of gases. The first catalyst is formed into a plasma in feed tube 22 by means 15 of the energy generated by the power supply 20 along with the hydrogen gas and the carbon-based gas. In this embodiment of the process of this invention, no substrate or solid catalyst particles are needed. Instead, the carbon nanofibers are produced on a steady state basis and, for that reason, it is necessary to supply apparatus 10 at one end of feed tube 22 with a catch basin, such as catch basin 46, in which the 20 fibers can be collected.

The carbon nanofibers formed by the above described processes of this invention have several applications. The high level of graphitization and crosslinking allows these fibers to efficiently conduct heat. By being able to efficiently conduct heat, these fibers can be used to provide thermal management systems such as heat 25 sinks for use in computers and printed circuit boards. The high aspect ratio allows these fibers to be used to shield electro-magnetic interference and to absorb radio frequency and microwave energy.

Specifically, the fibers formed by the method of this invention can be used to form high thermal conductivity cold plates for standard electronic module 30 (SEM) boards and other electronic cooling applications such as heat sinks for high

-10-

current devices such as MOS-Controlled Thyristors (MCTs). The fibers may also be used as an additive to provide improved strength and reinforcement to plastics, rubber, concrete, epoxies, and other materials. The carbon fibers can also be used as a replacement for carbon in rubber applications. At higher concentrations, the

5 fibers could be used to form an electrically conductive rubber. Because of their high electrical conductivity and small volume, the fibers can be used as an obscurant for microwaves, radio frequencies and other electromagnetic interferences. The fibers can also be used to form passive heat sinks for high heat flux devices. Electrically and thermally conductive adhesives and fillers can be formulated with the carbon

10 nanofibers as the key component. Finally, they can be used to absorb oil slicks on bodies of water because of their high surface area.

The carbon nanofibers formed by the process of this invention can be further processed to form a matrix material, such as a carbon-carbon matrix material or a carbon-epoxy matrix material, having an increased strength modulus, electrical

15 conductivity and thermal conductivity. To form a carbon-carbon matrix material, the carbon nanofibers can be formed by either of the above described methods. After formation, the fibers are not removed from reactor 12. Instead, the flow of gases into feed tube 22 is adjusted to form a second mixture of gases. This second mixture of gases is formulated to contain a higher concentration of the carbon-based gas.

20 Typically, the second mixture of gases will contain from about 0% to about 60% of the hydrogen gas and from about 40% to about 100% of the carbon-based gas. A person of skill in the art will appreciate that a different gas, such as one of those listed above, may be used as the carbon-based gas in forming the carbon matrix. However, by using the same gas for the carbon-based gas, the reaction is not

25 delayed by changes to the gas supply. Upon pyrolyzation, the increased concentration of carbon-based gas in the second mixture of gases forms a bulk carbon layer which infiltrates the carbon nanofibers to form a carbon-carbon matrix material. The matrix material is then removed from reactor 12 and can then be processed further for its desired use.

30 A matrix material may also be formed through the use of epoxy

materials. After the fibers have been formed on the substrate by means of the process described above, the substrate is removed from the reactor without removing the fibers from the substrate. The substrate is then used to form a portion of a mold used to make the matrix material. The remainder of the mold is formed so that it

5 incorporates the substrate. An epoxy material is then poured into the mold and so that it infiltrates the mass of fibers in the mold. The epoxy material is then cured so that the epoxy material and the carbon nanofibers form a matrix material. After the epoxy material has been cured, the matrix material is removed from the mold and the substrate. The resulting matrix material comprises a carbon-epoxy matrix material

10 which has high conductivity carbon nanofibers throughout its thickness. The carbon-epoxy matrix material can also be compression molded to a desired shape before being removed from the mold.

The method of forming carbon nanofibers of the present invention will now be illustrated by reference to the following example. The method is not intended

15 to be limited to the specific, exemplary materials below, but, rather, may be practiced generally by the principles delineated below.

Example

Approximately 0.1 grams of an iron sulfide catalyst was sprinkled onto a ceramic substrate. The ceramic substrate was then inserted into the feed tube of the

20 deposition apparatus. The pressure in the feed tube was reduced with a mechanical vacuum pump. A mixture of 50% hydrogen gas and 50% methane gas was then fed into the feed tube. Once the pressure in the feed tube reached 20 Torr, the power to the microwave reactor, an ASTEX microwave reactor, was turned on for approximately three minutes. The mixture of gases was formed into a plasma at a

25 substrate temperature of approximately 1000°C. The gas feed was then terminated along with the power to the reactor. The pressure in the feed tube was again reduced and the system was evacuated to prevent excess methane and hydrogen gas from escaping to the atmosphere. The substrate was then removed from the feed tube. Approximately 0.01 grams of carbon nanofibers were formed.

-12-

While certain representative embodiments and details have been shown for purposes of illustrating the invention, it will be apparent to those of skill in the art that various changes, modifications and alterations can be made to the process of this invention as disclosed herein without departing from the scope of the invention,  
5 which is defined in the appended claims.

## CLAIMS

1. A process for making carbon nanofibers in a reactor comprising the steps of:
  - providing, in a reactor, a first catalyst in the form of solid catalytic particles;
  - 5 applying a vacuum to the reactor to create a reduced pressure in the reactor;
  - feeding a first mixture of gases including a carbon-based gas into the reactor;
  - forming, from the carbon-based gas, a plasma containing carbon free-10 radical species; and
  - forming, in the presence of the catalytic particles, the carbon free-radical species into carbon nanofibers.
2. The process of claim 1 wherein the mixture of gases also includes hydrogen gas which is provided to inhibit pyrolytic fattening of the carbon nanofibers.
- 15 3. The process of claim 1 further including the step of feeding a growth catalyst gas into the reactor to cause the nanofibers to increase diametrically in size.
4. The process of claim 1 wherein the reduced pressure measures from about 10 Torr to about 100 Torr.
5. The process of claim 3 wherein the reduced pressure measures from about 20 20 Torr to about 50 Torr.
6. The process of claim 1 further including the steps of providing a substrate in the reactor and placing the catalytic particles on the substrate.

-14-

7. The process of claim 6 wherein the substrate is formed from an inert dielectric material.
8. The process of claim 1 wherein the carbon-based gas is formed into a plasma by an energy source selected from the group consisting of a microwave generator, 5 hot filament, electric discharge, and an RF generator.
9. The process of claim 2 wherein the carbon-based gas is selected from the group consisting of carbon dioxide, methane, ethane, propane, ethene, natural gas and coal derivative gases.
10. The process of claim 9 wherein the carbon-based gas is methane.
- 10 11. The process of claim 10 wherein the mixture of gases comprises from about 40% to about 90% hydrogen gas and from about 10% to about 40% methane gas.
12. The process of claim 1 further including the steps of:
  - increasing the concentration of the carbon-based gas in the first mixture of gases to form a second mixture of gases;
  - 15 pyrolyzing the second mixture of gases to deposit a bulk layer of carbon on the carbon nanofibers forming a carbon-carbon matrix material which contains carbon nanofibers throughout its thickness; and
  - removing the matrix material from the reactor.
13. The process of claim 12 wherein the first mixture of gases comprises from 20 about 40% to about 90% hydrogen gas and from about 10% to about 60% methane gas.

-15-

14. The process of claim 13 wherein the second mixture of gases comprises from about 0% to about 60% of hydrogen gas and from about 40% to about 100% of methane gas.
15. A process for making carbon nanofibers in a reactor comprising the steps of:
  - 5 applying a vacuum to the reactor to create a reduced pressure in the reactor;
  - feeding a mixture of gases including a carbon-based gas into the reactor;
  - feeding a catalyst gas into the reactor;
  - 10 forming, from the carbon-based gas, a plasma containing carbon free-radical species; and
  - forming, in the presence of the catalyst gas, the carbon free-radical species into carbon nanofibers.
16. The process of claim 15 wherein the mixture of gases also includes hydrogen gas which is provided to inhibit pyrolytic fattening of the carbon nanofibers.
17. The process of claim 15 further including the step of feeding a growth catalyst gas into the reactor to cause the fibers to increase diametrically in size.
18. The process of claim 15 wherein the reduced pressure measures from about 10 Torr to about 100 Torr.
- 20 19. The process of claim 18 wherein the reduced pressure measures from about 20 Torr to about 50 Torr.
20. The process of claim 15 wherein the carbon-based gas is formed into a plasma by an energy source selected from the group consisting of a microwave generator, hot filament, electric discharge, and an RF generator.

-16-

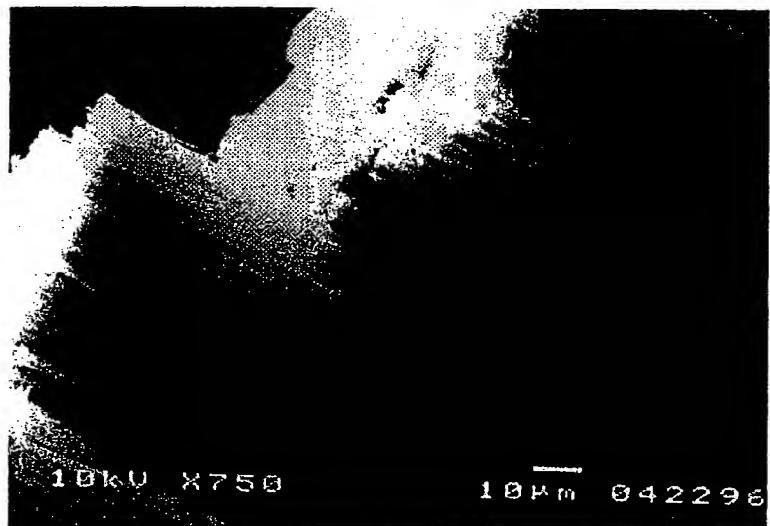
21. The process of claim 16 wherein the carbon-based gas is selected from the group consisting of carbon dioxide, methane, ethane, propane, ethene, natural gas and coal derivative gases.
22. The process of claim 21 wherein the mixture of gases comprises from about 5 40% to about 90% hydrogen gas and from about 10% to about 60% methane gas.
23. The process of claim 15 further including the steps of:
  - increasing the concentration of the carbon-based gas in the first mixture of gases to form a second mixture of gases;
  - pyrolyzing the second mixture of gases to deposit a bulk layer of carbon 10 on the carbon nanofibers forming a carbon-carbon matrix material which contains carbon nanofibers throughout its thickness; and
  - removing the matrix material from the reactor.
24. The process of claim 23 wherein the first mixture of gases comprises from about 40% to about 90% hydrogen gas and from about 10% to about 60% methane 15 gas.
25. The process of claim 24 wherein the second mixture of gases comprises from about 0% to about 60% of hydrogen gas and from about 40% to about 100% of methane.
26. A process for forming an carbon-epoxy matrix material comprising the steps of:
  - 20 providing, in a reactor, solid catalyst particles on a substrate;
  - feeding a mixture of gases including a hydrogen gas and a carbon-based gas into the reactor;
  - forming, from the carbon-based gas, a plasma containing carbon free-radical species;
  - 25 forming, in the presence of the catalytic particles, carbon nanofibers;

-17-

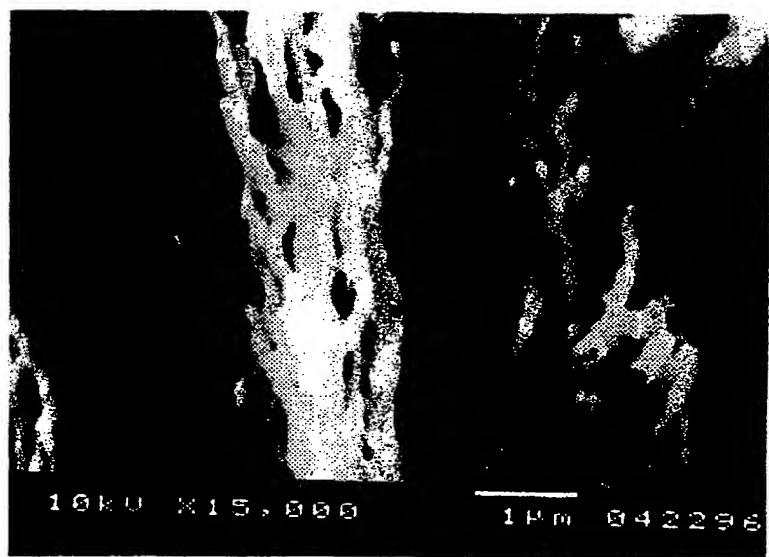
removing the substrate bearing the carbon nanofibers from the reactor;  
forming a mold in which a portion of the mold is formed by the substrate;  
infiltrating the mold with an epoxy composition to form a carbon-epoxy  
matrix material containing carbon nanofibers throughout its thickness; and  
5 removing the matrix material from the mold.

1/2

**FIG. 1**

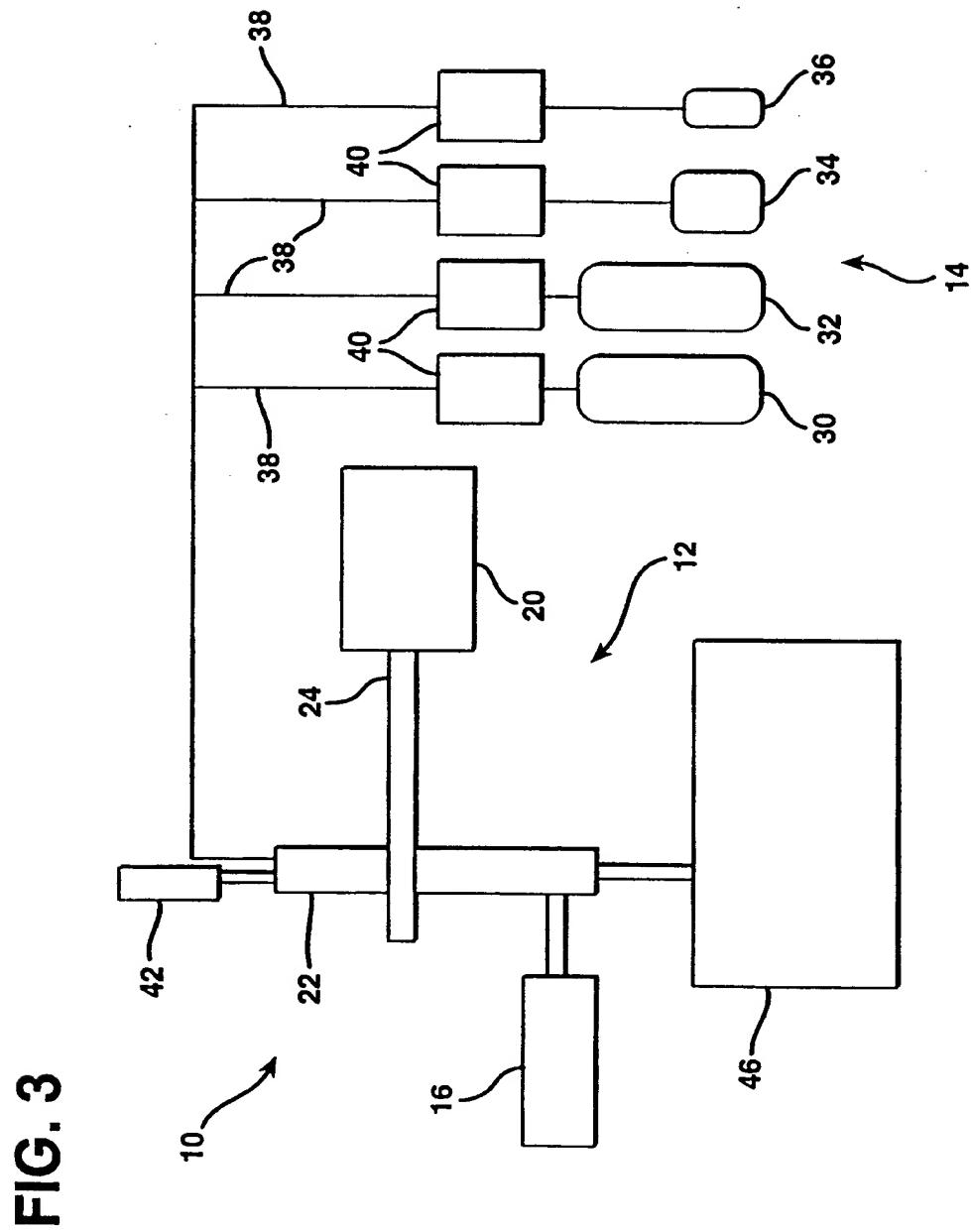


**FIG. 2**



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2/2



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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/10552

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 D01F9/127 D01F9/133

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D01F C04B C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 646 544 A (KEESMANN) 5 April 1995 (1995-04-05) column 2, line 48 -column 4, line 56; claims ----	1
A	DE 41 03 981 A (ROTHER ET AL.) 13 August 1992 (1992-08-13) claims ----	1
A	DE 42 08 719 A (SINDLHAUSER) 23 September 1993 (1993-09-23) claims ----	1,12
P,A	DE 197 40 389 A (KANZOW) 11 March 1999 (1999-03-11) claims -----	1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority, claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

4 October 1999

Date of mailing of the international search report

15/10/1999

Name and mailing address of the ISA

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## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/10552

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 646544 A	05-04-1995	DE 4333683 A AT 156779 T DE 59403715 D	06-04-1995 15-08-1997 18-09-1997
DE 4103981 A	13-08-1992	NONE	
DE 4208719 A	23-09-1993	NONE	
DE 19740389 A	11-03-1999	NONE	

37  
中华人民共和国国家知识产权局

邮政编码: 100031 北京市复兴门内大街 158 号远洋大厦 F10 层 中国国际贸易促进委员会专利商标事务所 刘志平					
申请号	01141294.1	部门及通知书类型	9 -D 		发文日期
申请人	佳能株式会社				
发明名称	电子发射器件, 电子源, 图像形成装置, 以及制造电子发射器件和 电子发射装置的方法				

## 第一次审查意见通知书

1.  依申请人提出的实审请求, 根据专利法第 35 条第 1 款的规定, 审查员对上述发明专利申请进行实质审查。

根据专利法第 35 条第 2 款的规定, 国家知识产权局决定自行对上述发明专利申请进行审查。

2.  申请人要求以其在:

日本 专利局的申请日 2000 年 9 月 1 日为优先权日, (Y011PP8  
日本 专利局的申请日 2001 年 8 月 24 日为优先权日,  
专利局的申请日 年 月 日为优先权日,  
专利局的申请日 年 月 日为优先权日,  
专利局的申请日 年 月 日为优先权日。

申请人已经提交了经原申请国受理机关证明的第一次提出的在先申请文件的副本。

申请人尚未提交经原申请国受理机关证明的第一次提出的在先申请文件的副本, 根据专利法第 30 条的规定视为未提出优先权要求。

3.  申请人于 年 月 日和 年 月 日提交了修改文件。

经审查, 申请人于: 年 月 日提交的 不符合实施细则第 51 条的规定。  
年 月 日提交的 不符合专利法第 33 条的规定。

4. 审查针对的申请文件:

原始申请文件。  审查是针对下述申请文件的

申请日提交的原始申请文件的权利要求第 项、说明书第 页、附图第 页;  
年 月 日提交的权利要求第 项、说明书第 页、附图第 页;  
年 月 日提交的权利要求第 项、说明书第 页、附图第 页;  
年 月 日提交的权利要求第 项、说明书第 页、附图第 页;  
年 月 日提交的说明书摘要, 年 月 日提交的摘要附图。

5.  本通知书是在未进行检索的情况下作出的。

本通知书是在进行了检索的情况下作出的。

本通知书引用下述对比文献(其编号在今后的审查过程中继续沿用):

回函请寄: 100088 北京市海淀区蓟门桥西土城路 6 号 国家知识产权局专利局受理处收  
21301 2002.7 (注: 凡寄给审查员个人的信函不具有法律效力)

编号	文件号或名称	公开日期
1	CN1181607A	1998年5月13日
2	W099/58748A1	1999年11月18日
3		年月日
4		年月日

6. 审查的结论性意见:

关于说明书:

- 申请的内容属于专利法第5条规定的不授予专利权的范围。
- 说明书不符合专利法第26条第3款的规定。
- 说明书不符合专利法第33条的规定。
- 说明书的撰写不符合实施细则第18条的规定。

关于权利要求书:

- 权利要求 1, 2, 4-6, 17, 18 不具备专利法第22条第2款规定的新颖性。
- 权利要求 3, 7-40 不具备专利法第22条第3款规定的创造性。
- 权利要求 \_\_\_\_\_ 不具备专利法第22条第4款规定的实用性。
- 权利要求 \_\_\_\_\_ 属于专利法第25条规定的不授予专利权的范围。
- 权利要求 \_\_\_\_\_ 不符合专利法第26条第4款的规定。
- 权利要求 \_\_\_\_\_ 不符合专利法第31条第1款的规定。
- 权利要求 \_\_\_\_\_ 不符合专利法第33条的规定。
- 权利要求 \_\_\_\_\_ 不符合专利法实施细则第2条第1款关于发明的定义。
- 权利要求 \_\_\_\_\_ 不符合专利法实施细则第13条第1款的规定。
- 权利要求 \_\_\_\_\_ 不符合专利法实施细则第20条的规定。
- 权利要求 \_\_\_\_\_ 不符合专利法实施细则第21条的规定。
- 权利要求 \_\_\_\_\_ 不符合专利法实施细则第22条的规定。
- 权利要求 \_\_\_\_\_ 不符合专利法实施细则第23条的规定。

上述结论性意见的具体分析见本通知书的正文部分。

7. 基于上述结论性意见, 审查员认为:

- 申请人应按照通知书正文部分提出的要求, 对申请文件进行修改。
- 申请人应在意见陈述书中论述其专利申请可以被授予专利权的理由, 并对通知书正文部分中指出的不符合规定之处进行修改, 否则将不能授予专利权。
- 专利申请中没有可以被授予专利权的实质性内容, 如果申请人没有陈述理由或者陈述理由不充分, 其申请将被驳回。

8. 申请人应注意下述事项:

- (1) 根据专利法第37条的规定, 申请人应在收到本通知书之日起的肆个月内陈述意见, 如果申请人无正当理由逾期不答复, 其申请将被视为撤回。
- (2) 申请人对其申请的修改应符合专利法第33条的规定, 修改文本应一式两份, 其格式应符合审查指南的有关规定。
- (3) 申请人的意见陈述书和/或修改文本应邮寄或递交国家知识产权局专利局受理处, 凡未邮寄或递交给受理处的文件不具备法律效力。
- (4) 未经预约, 申请人和/或代理人不得前来国家知识产权局专利局与审查员举行会晤。

9. 本通知书正文部分共有 5 页, 并附有下述附件:

- 引用的对比文件的复印件共 3 份 49 页。
- 审查 9 部 审查员 刘琼 审查部门业务专用章 \_\_\_\_\_  
(未加盖审查业务专用章的通知书不具备法律效力)

## 第一次审查意见通知书

本发明专利申请涉及一种电子发射器件、电子源、图像形成装置以及制造电子发射器件和电子发射装置的方法。经审查，具体审查意见如下：

1、权利要求 1 请求保护一种电子发射器件的制造方法，对比文件 1 公开了一种电子发射器件的制造方法，并披露了以下技术特征（见对比文件 1 附图 2 及说明书第 3-4 页）：在传导表面上布置一个阴极电极（见对比文件 1 附图标记 10），面对着阴极电极提供一电极（见对比文件 1 附图标记 2），在阴极电极上布置多件主要由碳构成的纤维（见对比文件 1 附图标记 11），在减压状态下对面对着阴极电极的电极施加一个电位，且该电位高于施加在阴极电极上的电位（见对比文件附图标记 30）。

由此可知，对比文件 1 公开了权利要求 1 的全部技术特征，二者所属技术领域相同，解决的技术问题相同，并采用了同样的技术手段，取得了相同的技术效果，因此，权利要求 1 相对于对比文件 1 不具备专利法第二十二条第二款所规定的新颖性。

2、权利要求 2 的附加技术特征为面对着阴极电极的电极为一脱离衬底的阳极电极。对比文件 1 公开了上述技术特征（见对比文件 1 附图标记 2）。因此，当其引用的权利要求 1 不具备新颖性时，权利要求 2 也不具备专利法第二十二条第二款所规定的新颖性。

3、权利要求 3 的附加技术特征为面对着阴极电极的电极为一脱离衬底表面上的阴极电极的一个引线电极。对比文件 1 的第二实施例中公开了上述技术特征（见对比文件 1 说明书第 6 页，附图 11，附图标记 14）。因此，当其引用的权利要求 1 不具备新颖性时，权利要求 3 不具备专利法第二十二条第三款所规定的创造性。

4、权利要求 4 的附加技术特征为对面对着阴极电极的电极施加一个电位的步骤是一个增加发射点数量的步骤。对比文件 1 公开了上述技术特征（见对比文件 1 说明书第 4 页第 2 段）。因此，当其引用的权利要求 1 不具备新颖性时，权利要求 4 不具备专利法第二十二条第二款所规定的新颖性。

5、权利要求 5 的附加技术特征为施加到面对着阴极电极的电极上的电位是从纤维上发射电子的电位。对比文件 1 公开了上述技术特征（见对比文件 1 说明书第 6 页第 2 段）。因此，当其引用的权利要求 1 不具备新颖性时，权利要求 5 不具备专利法第二十二条第二款所规定的新颖性。

6、权利要求 6 的附加技术特征为对面对着阴极电极的电极施加电位的步骤是在与纤维有化学或物理反应的一种气体环境中执行的。其作用是为了使主要由碳构成纤维与气体发生反应，使施加电位的纤维局部蚀刻。

对比文件 1 公开了施加电位的步骤是在氢气的气体环境中执行的（见对比文件 1 说明书第 4 页第 1 段）。其中对由多晶金刚石（相当于权利要求 6 的主要由碳构成的纤维）制成的场致发射体在氢气气氛下施加电压，可使发射体表面的碳与氢反应以使发射体的电子亲和势保持稳定状态。由于对比文件 1 公开的上述技术方案与本发明中技术方案相同，对比文件 1 中在氢气中对发射体施加电压，也同样会起到对被施加电压的发射体进行蚀刻的作用。

也就是说，对比文件 1 所公开的上述技术方案与权利要求 6 的技术方案相同，并且具有相同的技术效果。因此，当其引用的权利要求 1 不具备新颖性时，权利要求 6 不具备专利法第二十二条第二款所规定的新颖性。

7、权利要求 7 的附加技术特征为与纤维有化学反应的气体  $O_2$ 、 $H_2$ 、 $CO_2$ 、 $H_2O$ 。对比文件 1 公开了气体为  $H_2$ （见对比文件 1 说明书第 4 页第 1 段）。而  $O_2$ 、 $CO_2$ 、 $H_2O$  只是对  $H_2$  的等效替代，其作用都是为了使气体与纤维反应。因此，当其引用的权利要求 6 不具备新颖性时，权利要求 7 不具有突出的实质性特点和显著的进步，不具备专利法第二十二条第三款所规定的创造性。

8、权利要求 8 的附加技术特征为用来引入气体的压力等于或大于  $1 \times 10^{-4} Pa$ 。对比文件 1 公开了引入氢气时，氢气的分压力至少应为  $1 \times 10^{-6} Torr$ （见对比文件 1 说明书第 4 页第 1 段），约相当于  $1.33 \times 10^{-4} Pa$ 。因此，当其引用的权利要求 6 不具备新颖性时，权利要求 8 不具有突出的实质性特点和显著的进步，不具备专利法第二十二条第三款所规定的创造性。

9、权利要求 9 的附加技术特征为施加的电压为一脉冲电压。对比文件 1 公开了施加的电压为直流电压（见对比文件 1 说明书第 4 页第 1 段），而施加脉冲电压只是对直流电压的等效替代，其作用是为了使发射体在一定电压下发射电子。因此，当其引用的权利要求 6 不具备新颖性时，权利要求 9 不具有突出的实质性特点和显著的进步，不具备专利法第二十二条第三款所规定的创造性。

10、权利要求 10、11、12 的附加技术特征为纤维的形成方法。对比文件 2 公开了用于电子发射的碳纤维的制造方法，并披露了上述技术特征（见对比文件 2 说明书第 5 页第 27-30 行、第 6 页第 7-15 行）。由此可知，在对比文件 1 的基础上结合对比文件 2 得到权利要求 10、11、12 的技术方案对本领域技术人员来说是显而易见的。因此，当其分别引用的权利要求不具备新颖性或创造性时，权利要求 10、11、12 不具备突出的实质性特点和显著的进步，不具备专利法第二十二条第三款所规定的创造性。

11、权利要求 13 的附加技术特征为纤维是用一种石墨纳米纤维，碳纳米管，或者是非晶体碳纤维构成的。对比文件 2 公开了碳纳米纤维，而其他纤维构成只是对碳纳

米纤维的等效替代。因此，当其引用的权利要求 1 不具备新颖性时，权利要求 13 不具备专利法第二十二条第三款所规定的创造性。

12、权利要求 14、15、16 的附加技术特征为纤维包括一个或多个图形，多个图形被层叠在纤维的轴线上。对比文件 2 公开的碳纳米纤维也同样具有上述特征，因为，制造纤维的方法相同，纤维的结构特征也会相同。因此，当其分别引用的权利要求不具备新颖性或创造性时，权利要求 14、15、16 不具备突出的实质性特点和显著的进步，不具备专利法第二十二条第三款所规定的创造性。

13、权利要求 17 请求保护一种电子源的制造方法，对比文件 1 公开了一种电子源的制造方法（见对比文件 1 附图 13，说明书第 7 页），权利要求 17 与对比文件 1 的电子源制造方法的区别在于：权利要求 17 中电子源是用按照权利要求 1 到 16 之一的方法制成的许多电子发射器件布置而成的。

基于对权利要求 1 至 16 的评述，当权利要求 1 至 16 均不具备新颖性或创造性时，权利要求 17 也不具备专利法第二十二条第二款所规定的新颖性或专利法第二十二条第三款所规定的创造性。

14、权利要求 18 请求保护一种图像装置的制造方法，对比文件 1 公开了一种图像装置的制造方法（见对比文件 1 附图 13，说明书第 7 页），权利要求 18 与对比文件 1 的电子源制造方法的区别在于：权利要求 18 中电子源是用按照权利要求 17 的方法制成的。

基于对权利要求 17 的评述，当权利要求 17 不具备新颖性或创造性时，权利要求 18 也不具备专利法第二十二条第二款所规定的新颖性或专利法第二十二条第三款所规定的创造性。

15、权利要求 19 请求保护一种制造电子源的方法，对比文件 1 公开了一种制造电子源的方法，并披露了以下技术特征（见对比文件 1 附图 13，说明书第 7 页）：电子源由多个电子发射器件，每个电子发射器件有多个主要由碳构成的纤维以及用电路连接电子发射器件中的至少一个的多件导线（见对比文件 1 附图标记 11、x1、y1），在减压状态下从多个电子发射器件中的至少一个发射电子。

权利要求 19 与对比文件 1 的制造电子源的方法的区别在于：权利要求 19 中有对多个电子发射器件中的至少一部分施加一个电压，并且测量被施加电压的电子发射器件中的上述至少一部分的电气特性，以及根据测量结果降低多个电子发射器件之间在电气特性上的差别。

其中，上述测量一部分电子发射器件的电气特性的方法为本领域的公知常识。而对比文件 1 公开的制造电子源的方法中，在减压状态及氢气气氛下对一部分电子发射

器件与栅极之间施加电压可使上述一部分电子发射器件中的至少一个发射电子，虽然采用的发射体具有“均匀”的形状，但发射体在形状与长度也存在差别，因对比文件 1 公开的上述方法与本发明中降低多个电子发射器件之间在电气特性上的差别的方法相同，所以，对比文件 1 公开的上述方法同样也具有降低多个电子发射器件（发射体）之间在电气特性上的差别的作用。

由此可知，在对比文件 1 的基础上结合公知常识得到权利要求 19 的技术方案对本领域技术人员来说是显而易见的。因此，权利要求 19 不具有突出的实质性特点和显著的进步，不具备专利法第二十二条第三款所规定的创造性。

16、权利要求 20 至 26 的附加技术特征为对电子发射器件布置与选择、电子发射器件和引线电极之间电位的施加。对比文件 1 中公开用二维方式布置、选择电子发射器件，在阴极电极 10 和栅极 14 之间施加电压（见对比文件 1 附图 11、13，说明书第 6-7 页），而其他的方式只是对对比文件 1 中公开的方式的等效替代，并没有突出的实质性特点。因此，当其引用的权利要求不具备创造性时，权利要求 20 至 26 均不具备专利法第二十二条第三款所规定的创造性。

17、权利要求 27 至 30 的附加技术特征分别对应于权利要求 6 至 9 的附加技术特征，基于对权利要求 6 至 9 的评述，当权利要求 27 至 30 各自所引用的权利要求不具备创造性时，权利要求 27 至 30 均不具备专利法第二十二条第三款所规定的创造性。

18、权利要求 31 至 37 的附加技术特征分别对应于权利要求 10 至 16 的附加技术特征，基于对权利要求 10 至 16 的评述，当权利要求 31 至 37 各自所引用的权利要求不具备创造性时，权利要求 31 至 37 均不具备专利法第二十二条第三款所规定的创造性。

19、权利要求 38 请求保护一种图像形成装置的制造方法，对比文件 1 公开了一种图像形成装置的制造方法（见对比文件 1 附图 13，说明书第 7 页），权利要求 38 与对比文件 1 的电子源制造方法的区别在于：权利要求 38 中电子源是用按照权利要求 19 到 37 之一的方法制造的。

基于对权利要求 19 至 37 的评述，当权利要求 19 至 37 均不具备创造性时，权利要求 38 也不具备专利法第二十二条第三款所规定的创造性。

20、权利要求 39 的附加技术特征为图像形成装置是通过将设有图像形成部件的第一衬底和设有电子源的第二衬底密封粘接而获得的，并在密封粘接之前测量电子发射器件的电气特性。上述技术特征属于本领域的公知常识。因此，当其引用的权利要求 38 不具备创造性时，权利要求 39 也不具备专利法第二十二条第三款所规定的创造性。

21、权利要求 40 的附加技术特征为图像形成装置是通过将设有图像形成部件的第

一衬底和设有电子源的第二衬底密封粘接而获得的，而减少多个电子发射器件之间的电气特性差别的步骤是在密封粘接之前执行的。其中将上述第一衬底和第二衬底密封粘接而获得图像形成装置属于本领域的公知常识；而对比文件 1 公开了在密封了氢气的密封容器中通过在电子发射器件和栅极或阳极之间施加电压，该步骤可达到减少电子发射器件之间的电气特性差别的效果，因为其采用的技术方案与本发明中的一致。而本发明中减少多个电子发射器件之间的电气特性差别的步骤在衬底密封粘接前执行并未带来比上述步骤在衬底密封粘接后执行更好或意料不到的效果。因此，当其引用的权利要求 38 不具备创造性时，权利要求 40 不具有突出的实质性特点和显著的进步，不具备专利法第二十二条第三款所规定的创造性。

基于上述理由，本申请权利要求 1、2、4 至 6、17、18 不具备新颖性，权利要求 3、7 至 40 不具备创造性，同时说明书中也没有任何可以授予专利权的实质性内容，因而即使申请人对权利要求重新组合和/或根据说明书记载的内容作进一步的限定，本申请也不具备授予专利权的前景，如果申请人不能在本通知书指定的四个月答复期限内提出表明本申请具有新颖性和创造性的充分理由，本申请将被驳回。

## First Office Action (Brief)

The following references are cited in the Office Action:

Reference 1 (CN 1181607A; Priority document: JP 270786/96);

Reference 2 (WO 99/58748A1).

(1) The technical solution of claim 1 does not possess the novelty as required by Article 22 Paragraph 2 of the Patent Law.

All the technical features of claim 1 have been disclosed by Reference 1. Therefore, claim 1 is not allowable for the lack of novelty.

(2) The technical features of claim 2 have been disclosed by Reference 1, therefore, claim 2 is not allowable for the lack of novelty, according to Article 22 Paragraph 2 of the Patent Law.

(3) The technical features of claim 3 have been disclosed by Reference 1, therefore, claim 3 is not allowable for the lack of inventiveness, according to Article 22 Paragraph 3 of the Patent Law.

(4) The technical features of claim 4 have been disclosed by Reference 1, therefore, claim 4 is not allowable for the lack of

novelty, according to Article 22 Paragraph 2 of the Patent Law.

(5) The technical features of claim 5 have been disclosed by Reference 1, therefore, claim 5 is not allowable for the lack of novelty, according to Article 22 Paragraph 2 of the Patent Law.

(6) The technical features of claim 6 have been disclosed by Reference 1, therefore, claim 6 is not allowable for the lack of novelty, according to Article 22 Paragraph 2 of the Patent Law.

(7) The technical features of claim 7 have been disclosed by Reference 1, therefore, claim 7 is not allowable for the lack of inventiveness, according to Article 22 Paragraph 3 of the Patent Law.

(8) The technical features of claim 8 have been disclosed by Reference 1, therefore, claim 8 is not allowable for the lack of inventiveness, according to Article 22 Paragraph 3 of the Patent Law.

(9) The technical features of claim 9 have been disclosed by Reference 1, therefore, claim 9 is not allowable for the lack of inventiveness, according to Article 22 Paragraph 3 of the Patent Law.

(10) The technical features of claims 10-12 have been disclosed by Reference 2, therefore, claims 10-12 are not allowable for the lack of inventiveness, according to Article 22 Paragraph 3 of

the Patent Law.

(11) The technical features of claim 13 have been disclosed by Reference 2, therefore, claim 13 is not allowable for the lack of inventiveness, according to Article 22 Paragraph 3 of the Patent Law.

(12) The technical features of claims 14-16 have been disclosed by Reference 2, therefore, claims 14-16 are not allowable for the lack of inventiveness, according to Article 22 Paragraph 3 of the Patent Law.

(13) The technical features of claim 17 have been disclosed by Reference 1, therefore, claim 17 is not allowable for the lack of inventiveness, according to Article 22 Paragraph 3 of the Patent Law.

(14) The technical features of claim 18 have been disclosed by Reference 1, therefore, claim 18 is not allowable for the lack of inventiveness, according to Article 22 Paragraph 3 of the Patent Law.

(15) The technical features of claim 19 have been disclosed by Reference 1, therefore, claim 19 is not allowable for the lack of inventiveness, according to Article 22 Paragraph 3 of the Patent Law.

(16) The technical features of claims 20-26 have been

disclosed by Reference 1, therefore, claims 20-26 are not allowable for the lack of inventiveness, according to Article 22 Paragraph 3 of the Patent Law.

(17) The technical features of claims 27-30 have been disclosed by Reference 1, therefore, claims 27-30 are not allowable for the lack of inventiveness, according to Article 22 Paragraph 3 of the Patent Law.

(18) The technical features of claims 31-37 have been disclosed by Reference 2, therefore, claims 31-37 are not allowable for the lack of inventiveness, according to Article 22 Paragraph 3 of the Patent Law.

(19) The technical features of claim 38 have been disclosed by Reference 1, therefore, claim 38 is not allowable for the lack of inventiveness, according to Article 22 Paragraph 3 of the Patent Law.

(20) The technical features of claim 39 are general knowledge in the art, therefore, claim 39 is not allowable for the lack of inventiveness, according to Article 22 Paragraph 3 of the Patent Law.

(21) The technical features of claim 40 have been disclosed by Reference 1, therefore, claim 40 is not allowable for the lack of inventiveness, according to Article 22 Paragraph 3 of the Patent

**Law.**

For the above reasons, all of the claims are not allowable for the lack of novelty or inventiveness. And the application will be rejected.